Derivation and analysis of ceramic materials based on $BaTiO_3$ by using standard ceramic technology

Valentin Kolev, Anka Zeglova, Ivailo Lazarov

Ceramic materials based on $BaTiO_3$ have been derived by using a standard ceramic technology. Various quantities of H_3BO_3 and Bi_2O_3 have been added in order to lower the temperature of synthesis. For the researched material, an X-ray diffraction analysis was carried out. The dependencies of the density, the relative permittivity and the contraction on the temperature of sintering, have been obtained. The addition of H_3BO_3 leads to higher density values, but the dielectric permeability is not high. The addition of Bi_2O_3 assures a liquid stage during the synthesis and supports the solid-phase reactions. The highest relative dielectric permeability values were obtained for the ceramic material by simultaneous addition of H_3BO_3 and Bi_2O_3

Keywords: *barium titanate, layered capacitors, nonlinear ceramics*

Получаване и изследване на керамични материали на основата на $BaTiO_3$ по стандартна керамична технология (Валентин Колев, Анка Жеглова, Ивайло Лазаров) *Керамични материали на основата на $BaTiO_3$ са получени чрез използване на стандартна керамична технология. За намаляване температурата на синтез са използвани различни количества H_3BO_3 и Bi_2O_3. На изследваните материали е проведен рентгеноструктурен анализ. Получени са зависимостите на плътността, относителната диелектрична проницаемост и свиването в зависимост от температурата на синтез. Прибавянето на H_3BO_3 води до добри стойности на плътността, но диелектричната проницаемост не е висока. Добавката Bi_2O_3 обезпечава течна фаза при синтеза и улеснява твърдофазните реакции. Най-високи стойности за относителната диелектрична проницаемост са получени при керамични материали с едновременно добавени H_3BO_3 и Bi_2O_3*

Introduction

Barium titanate is one of the most used and well-studied ferroelectrics. It has a cubic structure (m3m) at a temperature above 120° C. At a lower temperature, it is sequentially converted in three ferroelectric phases. At first it has a tetragonal structure (4 mm), then a rhombohedral one (mm) at 5° C and at -90° C its structure is triagonal (3m). The polar axes in these three ferroelectric phases are respectively [001], [011] and [111]. The transitions are type I and are accompanied by abrupt changes in the relative permittivity [1].

The tetragonal phase of barium titanate is used for a number of electronic components that use its ferroelectric properties. The cubic phase which is not ferroelectric, has a high dielectric constant and is suitable for capacitors [2]. High values of capacities are achieved by the obtaining of layered capacitors. The materials used for electrodes for such capacitors require a reduced temperature of sintering of the $BaTiO_3$ ceramic.

Upon the derivation of ferroelectric ceramic materials, the addition of various amounts of alloying materials such as Zr [3], Hf [4], Ce [5], Sn [6], etc. is used to manage their properties. The paper [7] presents an approach for obtaining multiferroic properties in co-doped (Zn:Mn) $BaTiO_3$ near room temperature. Bhatia have studied the influence of a new lead-free Fe/Li incorporated H-Bt, prepared by the solid state reaction method and compared it with pure hexagonal barium titanate [8]. The aim of the research in [9] is to find out the structural modifications and corresponding change in properties of $BaTiO_3$, when a small amount of glass was added. Lead oxide (PbO) in powder form was used as glass for the doping.

The alloying materials influence the homogeneity of the compositions, the particle size of the ceramic, the density, the structural defects as well as the electric properties such as dielectric constant, tangent of dielectric loss etc. They also affect the Curie temperature [10]. The technological factors during the derivation of the ceramics, affect its characteristics [2].

Various authors have used different alloying materials for lowering the temperature of sintering of the ceramics of $BaTiO_3$. Chi-Shung His added borosilicate glass and LiF [11] and Hamid Naghib-zaden lowers the temperature of synthesis via doped ZnO-B_2O_3-Li_2O-Nb_2O_5-Co_2O_3.

The objective of the present study is to reduce the sintering temperature of the ceramics of $BaTiO_3$ by adding various alloying materials.

Experimental

To achieve the above mentioned objective, ceramic materials of the composition of the base 6 of $BaTiO_3$ with different alloying materials have been obtained and tested.

As starting components for the preparation of the ceramic composition, the following components have been used: $BaCO_3$, $SrCO_3$, TiO_2, H_3BO_3 and Bi_2O_3.

The following compounds have been studied:

I- $Ba_{0,9}$ $Sr_{0,1}TiO_3$,

II- $Ba_{0,8}$ $Sr_{0,2}TiO_3$

III- $Ba_{0,8}$ $Sr_{0,2}TiO_3$ + 5wt % H_3BO_3

IV- $Ba_{0,8}Sr_{0,2}TiO_3$+5wt%H_3BO_3+ 15wt% Bi_2O_3

V- $Ba_{0,8}$ $Sr_{0,2}TiO_3$ + 15wt % Bi_2O_3

VI- $Ba_{0,8}$ $Sr_{0,2}TiO_3$ + 7,5wt % Bi_2O_3

The starting powders in the required amounts have been homogenized in 3% of polyvinyl alcohol solution for 4 hours at planetary mill Pulvirisete 5. After drying of the materials, disks with diameter 11 mm and a thickness of 2-3 mm have been formed, by compression at a pressure 300 MPa. Synthesis was carried out in air for 3 hours at 5 different temperatures of: 1025°C, 1050°C, 1100°C, 1125°C and 1150°C. After a mechanical treatment, silver electrodes have been formed by applying a coating of silver paste on the ceramic disks.

Analysis of the results

X-ray diffractograms

X-ray diffractograms of the samples were recorded on x- diffractometer by using Cu-Kα radiations (λ=1.541874 À) in the range $15^o \leq 2\theta \leq 105^o$, at a scanning rate of 0.05o/s.

Figure 1 shows the composition I at Tc = 1150°C. A solid solution $Ba_{0,9}Sr_{0,1}TiO_3$ with tetragonal structure, has been synthesized.

X-ray diffractogram of composition II $Ba_{0,8}Sr_{0,2}TiO_3$ is presented in Figure 2. The increase of the quantity of SrO_2 leads to an increase of the intensity of the peak (reflex) at 2Θ=230, as well as to a new peak (reflex) at 2Θ=280. ($BaTi_4O_9$has been synthesized).It is a solid solution of barium strontium titanate and $BaTi_4O_9$

The derived X-ray diffractogram is similar to the one for compound I.

Figure 3 shows the diffractogram of the composition $Ba_{0,8}$ $Sr_{0,2}TiO_3$ + 5wt% H_3BO_3 + 15wt% Bi_2O_3 at temperature of synthesis 1150 ^{0}C .

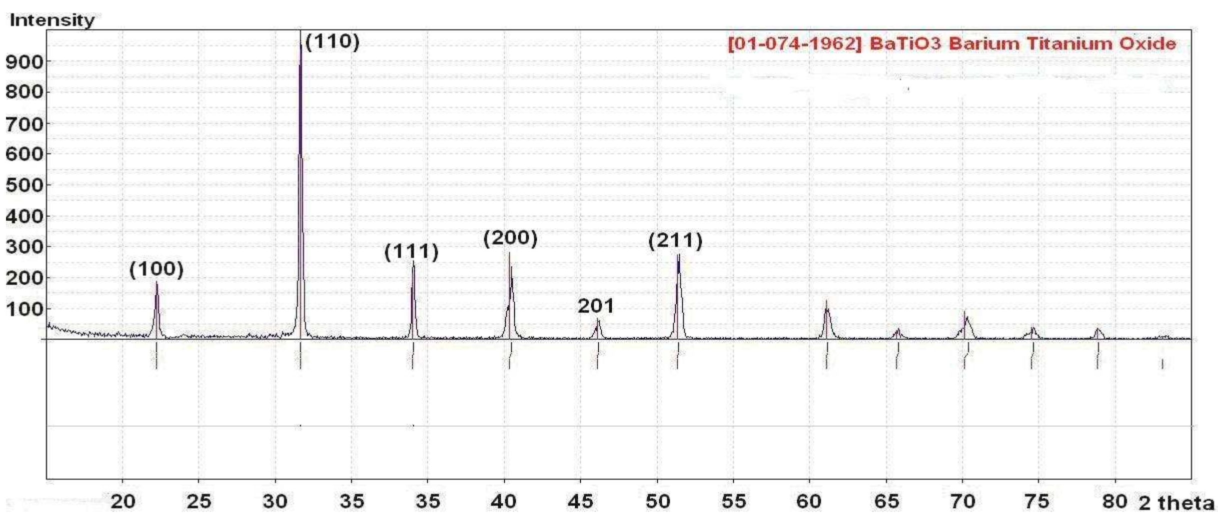

Fig. 1. X-ray diffractogram of composition $Ba_{0,9}Sr_{0,1}$ TiO_3 at temperature of synthesis 1150^{0}C.

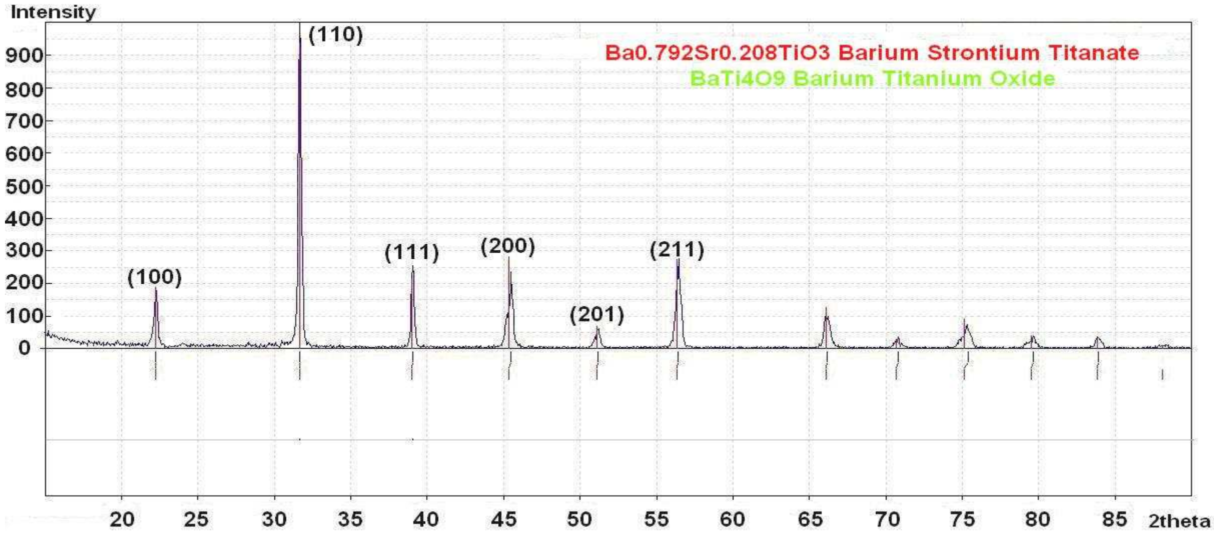

Fig.2. X-ray diffractogram of composition $Ba_{0,8}Sr_{0,2}TiO_3$ at temperature of synthesis 1150^0C.

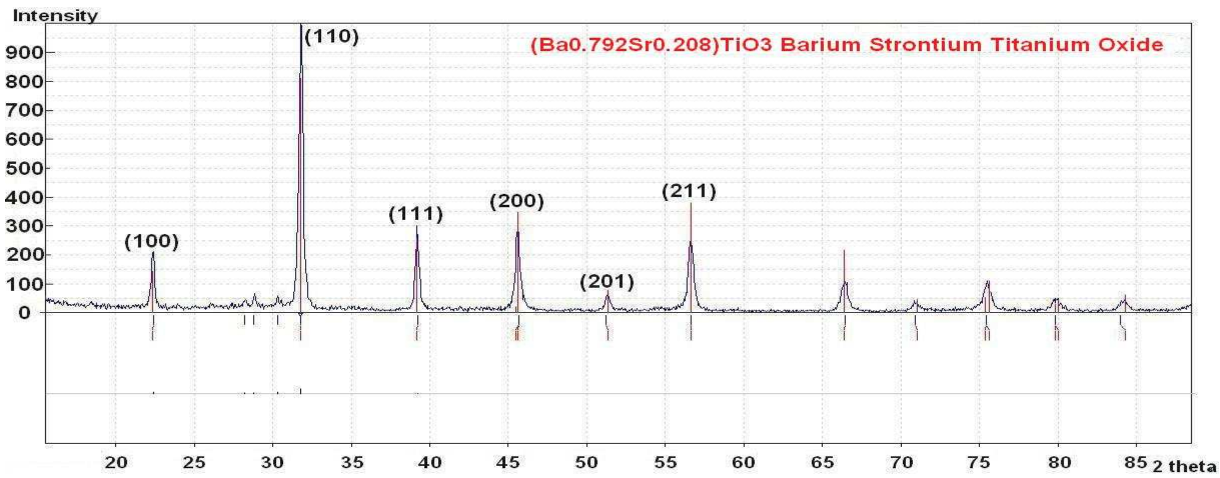

Fig.3. X-ray diffractogram of composition $Ba_{0,8}Sr_{0,2}TiO_3$ + 5wt% H_3BO_3 + 15wt% Bi_2O_3 at temperature of synthesis 1150^0C.

Density and relative contraction

The results of the measured density are presented in Table № 1 with different sintering temperatures. For all analyzed compositions the density increases as the temperature of synthesis increases. The highest density is obtained for the compositions IV and VI, which contain Bi_2O_3. The lowest density configurations are II and III. The addition of H_3BO_3 does not improve the quality of the ceramic material. Compositions I and II contain $SrTiO_3$, which is known to affect of the Curie temperature and the coefficient of non-linearity, but at temperatures of synthesis up to 1150 ^0C it is unable to assist in obtaining a dense ceramic.

In Table 2 show the relative shrinkage of the materials according to the temperature of synthesis. Compositions containing $SrTiO_3$, without the addition of Bi_2O_3, do not shrink but expand. This indicates that the temperature of the synthesis is not high enough for the complete course of the solid phase reactions. The increase of the temperature of synthesis leads to an increased of the relative shrinkage. It is likely that at a higher temperature, the shrinkage will be greater. In correlation with the density, compositions IV and VI shrink the most

Table 1

Dependence of the density of the ceramic materials on the temperature of synthesis

Composition	Density, $g.10^{-3}/mm^3$				
Sintering temperatures	1025^0 C	1050^0 C	1100^0 C	1125^0 C	1150^0 C
I	0,71	0,89	1,82	1,98	2,4
II	1,51	1,54	1,56	1,59	1,63
III	1,63	1,72	1,82	1,83	1,85
IV	2,64	2,93	3,38	3,47	3,68
V	2,34	2,41	2,71	2,79	2,91
VI	2,57	2,89	3,38	3,52	3,63

Table 2

Dependence of the relative shrinkage of the ceramic materials on the temperature of synthesis

Composition	Relative shrinkage,%				
Sintering temperatures	1025^0 C	1050^0 C	1100^0 C	1125^0 C	1150^0 C
I	-13,64	-12,75	-7,92	-5,24	-1,36
II	-14,02	-13,64	-13,64	-13,15	-12,73
III	-9,85	-9,09	-7,27	-6,85	-6,65
IV	2,43	4,54	9,09	10,04	11,82
V	-2,43	0	- 4,54	- 5,67	- 6,36
VI	- 1,36	- 4,54	- 9,09	- 10,04	- 11,8

Relative permittivity

The relative permittivity of the resulting materials is presented in Figure 4 and Table 3.

As expected the ceramic compositions with the highest density (IV and VI), have highest relative permittivity. For composition II, the permeability decreases with the increase of the temperature of synthesis, while for composition III it remains constant.

Dependence of the relative permittivity on the temperature of composition $Ba_{0,8}$ $Sr_{0,2}TiO_3$ + 5wt % H_3BO_3 is show in Figure 5. For all temperatures of sintering, a renounced phase transition around 115°C was observed. This temperature is lower than the Curie point for clean barium titanate. The phase transition of ceramic material sintered at 1150°C has been observed most clearly. At this temperature the relative permittivity reaches its maximum value.

Conclusion

Based on the above mentioned studies, we can conclude the following:

- The increase of the temperature of synthesis leads to an increase of the density and the relative shrinkage of the relative permittivity
- The addition of $SrTiO_3$ to ceramics of barium titanate does not lead to a reduction in the temperature of synthesis. The derived

materials have low density and low permittivity;

- Better results is obtained when H_3BO_3 is added to a strontium-containing ceramics, but the values of permittivity are very low;
- When Bi_2O_3 is added, both the density and the dielectric constant of the ceramic materials based on $BaTiO_3$, significantly increase. Bi_2O_3 has a low melting point to form a liquid phase which facilitates the solid-phase reactions.
- Top quality materials are obtained by the simultaneous addition of Bi_2O_3 and H_3BO_3 to $BaTiO_3$.

Table 3

Dependence of the relative permittivity on the temperature of synthesis

Composition	Relative permittivity				
Sintering temperatures	1025^0 C	1050^0 C	1100^0 C	1125^0 C	1150^0 C
I	143	158	213	292	385
II	184	176	157	138	110
III	112	115	118	120	122
IV	189	227	346	448	506
V	173	213	287	342	384
VI	216	276	357	393	440

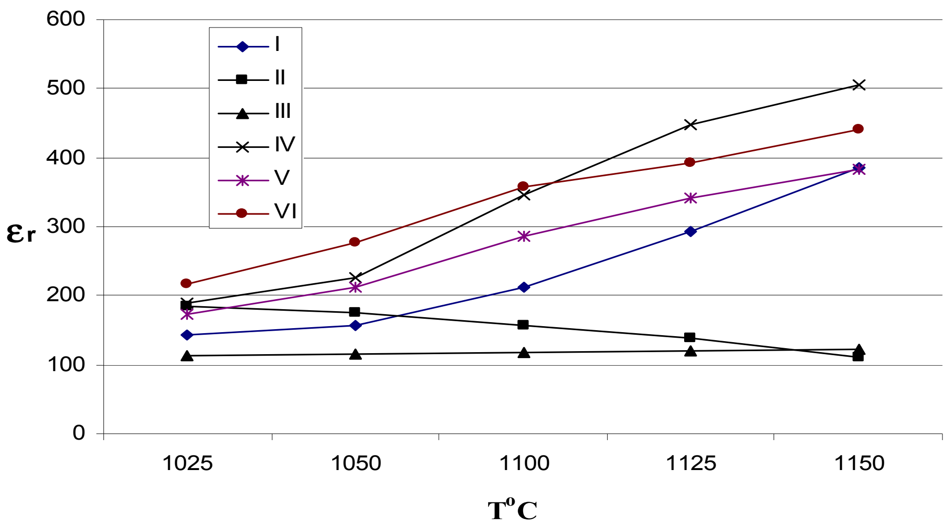

Fig.4. Dependence of the relative permittivity on the temperature of synthesis.

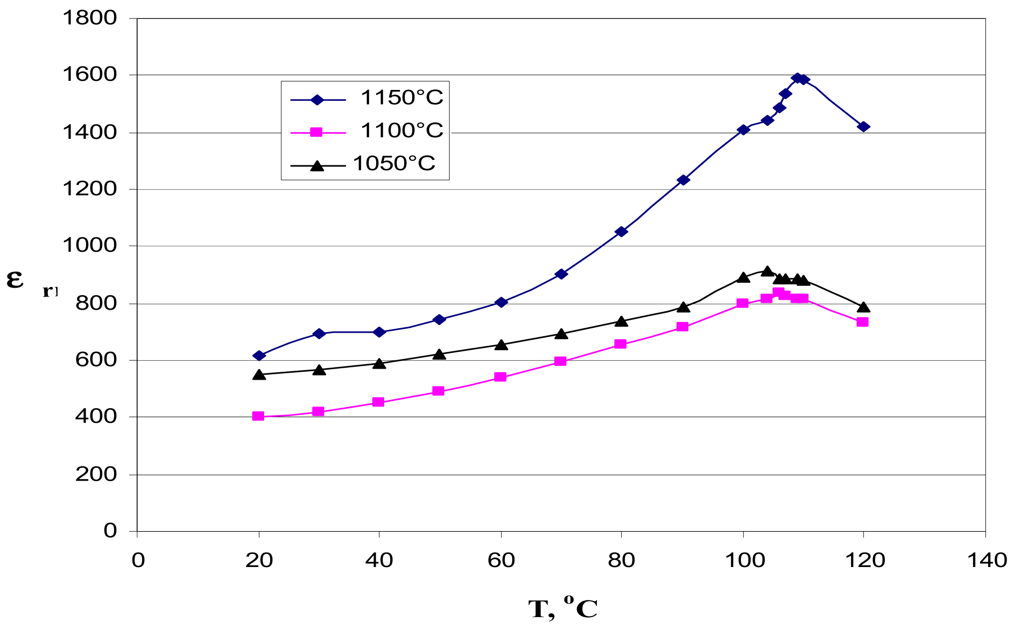

Fig.5. Dependence of the relative permittivity on the temperature of composition $Ba_{0,8}Sr_{0,2}TiO_3$ + 5wt % H_3BO_3.

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Assoc Prof. Dr. Valentin Kolev – PhD *in Technical university of Sofia, Faculty of Electrical Engineering, Head of Chair "Electrical power engineering". He completed his education from Technical University of Sofia. Main areas of research are Technic of High Voltage Engineering.*

tel.:+359882142506 e-mail: vkolev@tu-sofia.bg

Assoc. Prof. Anka Zheglova - PhD *in Department of Fundamentals of Electrical and Power Engineering, Faculty of Electrical Engineering and Electronics, Technical University – Gabrovo. She completed hir education from Electrical Engineering University –Sankt Peterburg, Russia. Main areas of research are Materials science and technology, especially – ceramics materials.*

tel.+359879003368 e-mail: anyany@tugab.bg.

Ivailo Lazarov*- assistant* ***PhD*** *in Department of Fundamentals of Electrical and Power Engineering, Faculty of Electrical Engineering and Electronics, Technical University – Gabrovo. He completed his education from Technical University – Gabrovo. Main areas of research are Materials science and technology.*

tel.+35966827322 e-mail:iv.lazarov@mail.bg

Received on: 30.06.2015